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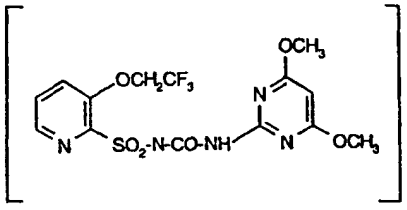

$$M^{m+} \bullet L_r \bullet [H_2O]_s \quad (I)$$

(57) Abstract

Compounds of formula (I) wherein M is an alkali metal or an alkaline earth metal; n is 1 or 2; r and s, independently of one another, are 0, 1/2, 1, 1,5, 2, 2,5 or 3; and L is ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N–methyl–2–pyrrolidone, acetone, butanone, methylene chloride, trichloromethane, trichloroethane, tetrahydrofuran, diethylether, 1, 2–dimethoxyethane, dioxane, methyl–tert.–butylether, chlorobenzene, toluene or xylene, with the provision that r is other than 1,5 if L is dioxane and s is 0, are suitable for use as herbicides.

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SULFONYLUREA SALTS AS HERBICIDES

The present invention relates to novel herbicidally active pyridylsulfonylurea salts, to processes for their preparation, to compositions comprising said compounds, and to the use thereof for controlling weeds, in particular in crops of cultivated plants or for inhibiting plant growth.

Various crystal forms (modifications) of a chemical compound can exhibit very different physical properties, which may lead to unforeseeable problems during technical preparation and processing of these compounds.

The characteristics of crystal modifications frequently have a crucial influence on the separating ability (filtration), stirrability (crystal volume), surface activity (foaming), rate of drying, solubility, quality, formulating ability and storage stability (e.g. hygroscopy) of for example pharmaceutically and agronomically active compounds. For example, the grinding and formulating properties (e.g. tabletting) of products may be completely different, depending on the respective crystal modification (Pharm. Ind. 59, 2, 165-169 (1997)). Since, in the various stages of synthesis of a preparation process, different physical properties of the respective synthesis products are of importance, it is especially advantageous to find the optimally suited crystal form for the respective stage of synthesis.

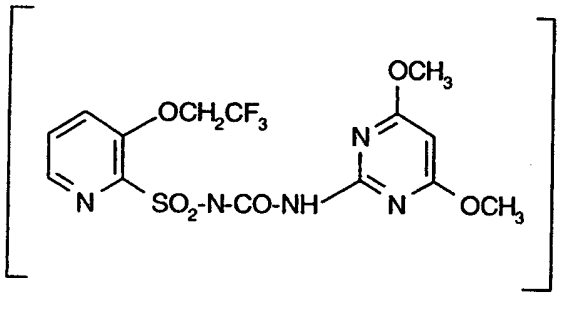
Furthermore, a modification can suddenly transform into another undesired modification under certain thermodynamic conditions. These transformations may be reversible or irreversible and are generally not predictable.

Pyridylsulfonylurea salts with herbicidal activity are described for example in WO 97/41112. From the description of the preparation of the sodium salt of N-[3-(2-trifluoroethoxy)-pyridin-2-yl-sulfonyl]-N'-(4,6-dimethoxy-pyrimidin-2-yl)-urea mentioned in this document, however, it is not possible to deduce whether amorphous or crystalline products are obtained, or which crystal modification or mixtures of modifications are produced, since physical parameters such as temperature, humidity and pressure which are crucial for targeted synthesis are not mentioned. In addition, the melting point only characterises a crystal structure insufficiently, since during the measuring procedure the original crystal modification can be transformed into another modification or into mixtures of modifications. Moreover, the melting point may

be falsified by the presence of amorphous material and by the evaporation of solvatising solvent.

It is therefore the aim of the present invention to specifically provide crystal modifications of salts of N-[3-(2-trifluoroethoxy)-pyridin-2-yl-sulfonyl]-N'-(4,6-dimethoxy-pyrimidin-2-yl)-urea, the properties of which substantially improve the technical preparation of the active ingredient, its formulation and its storability.

Accordingly, the present invention relates to compounds of formula I



$$M^{n+} \bullet L_r \bullet [H_2O]_s \quad (I),$$

wherein

M is an alkali metal or an alkaline earth metal;

n is 1 or 2;

r and s, independently of one another, are 0, ½, 1, 1½, 2, 2½ or 3; and

L is ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane, trichloroethane, tetrahydrofuran, diethylether, 1,2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, with the provision that r is other than 1½ if L is dioxane and s is 0.

M as an alkali metal and as an alkaline earth metal in the context of the present invention is preferably sodium, potassium, magnesium and calcium.

The present invention includes all crystal modifications that may be formed by the compounds of formula I.

Preferred compounds of formula I are characterised in that L is dioxane, tetrahydrofuran or water.

Further preference is given to compounds of formula I, in which n is 1, and M is especially sodium.

Also preferred are compounds of formula I, in which M is sodium, n is 1, r is 0 and s is 0.

Also notable is the amorphous solid form of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0. For example, this form can be used to produce other crystal modifications, such as the C-modification. The amorphous form therefore forms a further object of the present invention.

Particularly preferred individual compounds falling within the scope of formula I are the compounds selected from

- the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 10.0/average; 9.2/strong; 8.6/very weak; 8.1/weak; 7.2/strong; 6.9/strong; 6.4/average; 5.82/strong; 5.75/strong; 5.64/very strong; 5.53/very weak; 5.13/average; 4.97/very strong; 4.65/average; 4.30/very strong; 4.22/weak; 4.15/very weak; 4.02/weak; 3.94/weak; 3.79/average; 3.73/weak; 3.68/average; 3.61/weak; 3.58/weak; 3.52/very strong; 3.42/very weak; 3.37/weak; 3.31/very weak; 3.27/very weak; 3.23/weak; 3.18/average; 3.08/very weak; 3.03/very weak; 2.95/very weak; 2.87/strong; 2.82/very weak; 2.79/very weak; 2.73/very weak; 2.68/very weak; 2.65/very weak; 2.63/very weak; 2.60/weak; 2.57/weak;

- the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0. characterised by the X-ray powder pattern with d[Å]/intensity: 15.7/weak; 10.2/very strong; 8.2/weak; 7.8/weak; 7.3/weak; 6.7/weak; 6.5/very weak; 6.2/average; 5.64/very weak; 5.53/weak; 5.42/weak; 5.09/weak; 4.96/average; 4.86/very weak; 4.60/average; 4.37/average; 4.24/weak; 4.11/very strong; 3.95/very weak; 3.90/weak; 3.81/very weak; 3.71/average; 3.62/weak; 3.52/very weak; 3.43/strong; 3.37/weak; 3.32/very weak; 3.27/weak; 2.94/very weak; 2.82/average;

- the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, characterised by the X-ray powder pattern with d[Å]/intensity: 13.4/weak; 10.1/very

weak; 9.3/very strong; 7.8/weak; 6.9/very weak; 6.7/very weak; 5.63/very weak; 5.35/average; 4.66/weak; 4.44/very weak; 4.35/weak; 4.12/strong; 3.94/strong; 3.87/very weak; 3.76/weak; 3.61/average; 3.49/very weak; 3.40/very weak;

- the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 13.1/average; 11.0/very strong; 8.8/weak; 7.7/very strong; 7.2/very strong; 7.0/weak; 6.4/weak; 6.2/strong; 5.96/weak; 5.90/weak; 5.64/strong; 5.47/weak; 5.34/average; 5.19/weak; 4.79/weak; 4.74/average; 4.64/very weak; 4.55/strong; 4.47/weak; 4.35/strong; 4.26/average; 4.13/weak; 4.06/very weak; 3.92/very strong; 3.87/weak; 3.79/very strong; 3.67/weak; 3.61/average; 3.58/strong; 3.47/weak; 3.32/very weak; 3.24/average; 3.14/weak; 3.12/weak; 3.07/weak; 3.04/strong; 2.97/very weak; 2.92/very weak; 2.88/weak; 2.82/weak; 2.77/very weak; 2.74/very weak; 2.69/weak; 2.66/very weak; and

- the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 1.6/weak; 9.8/very weak; 8.0/very strong; 7.6/average; 6.7/strong; 6.4/very weak; 6.3/weak; 6.1/very weak; 5.80/average; 5.66/very weak; 5.47/strong; 5.12/very weak; 5.08/very weak; 4.84/weak; 4.76/weak; 4.47/strong; 4.40/weak; 4.21/average; 4.19/average; 4.15/very weak; 4.00/very weak; 3.93/very weak; 3.84/average; 3.72/very strong; 3.58/average; 3.52/average; 3.32/very weak; 3.28/very weak; 3.25/very weak; 3.11/very weak; 3.07/very weak; 2.95/very weak; 2.86/weak; 2.82/very weak; 2.75/very weak; 2.57/weak; 2.49/very weak.

Special significance is attributed to the B-modification.

Preference is also given to
- the K-modification of the compound of formulal I, in which M is sodium, n is 1, r is 0 and s is 0, produced by drying the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification), at a temperature of 35°C to 65°C in a vacuum.

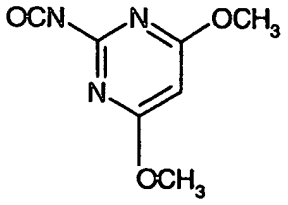
- the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, produced either by

contact of the essentially amorphous form (A-modification) by air of 98% relative humidity or mixing the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, with water in a ratio of water to K-modification of 0.1 : 1 to 0.4 : 1 and separating and drying the product obtained at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;

- the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, produced by adding water to the compound of formula I, in which M is sodium, n is 1, and L, r and s are defined as for formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, filtering and drying the residue of filtration at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars, or preferably produced by adding water to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (K-modification), or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification) or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1 (I-modification), or to the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1 (C-modification), in a ratio of water to the K, J, I or C modification of 0.5 : 1 to 20 : 1, filtering and drying the residue of filtration at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

In the K-modification, the surprisingly high thermodynamic stability and the non-hygroscopic properties are especially notable. The B-modification similarly has high stability in the presence of water. This property is of advantage especially in the preparation of formulations of the active ingredient. Particular importance is therefore placed on the K and B modifications.

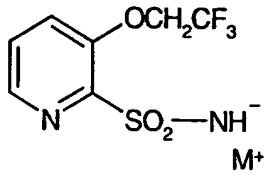
The compounds of formula I may be produced by a generally known process, whereby a compound of formula II



(II)

in ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane,

trichloroethane, tetrahydrofuran, diethylether, 1,2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, is reacted with a compound of formula III

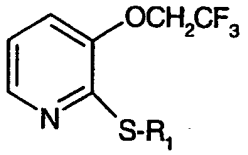


(III)

wherein M is as defined under formula I.

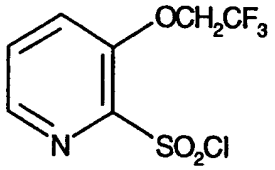
The compound of formula II is reacted with the compound of formula III at temperatures of -20°C to 180°C, a temperature range of 30–80°C being preferred. The compounds of formulae II and III can be used in equivalent stoichiometric quantities, although a slight excess of isocyanate may be of advantage.

The preparation of the starting compound of formula II is described, for example, in EP-A-0 232 067, page 29. The compounds of formula III may be prepared, for example, by converting the compound of formula IV



(IV),

wherein R_1 is -CH_2-phenyl or isopropyl, by means of aqueous chlorination, into the compound of formula V



(V)

This compound is treated with aqueous ammonia, and the resulting sulfonamide is then reacted with 30% sodium methylate. Such reactions are known, and are familiar to the specialist.

Preferred crystal modifications of the compounds of formula I are produced by processes that have been specially developed for the present invention. These processes therefore form a further object of the present invention.

The process for the preparation of the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0, is thus characterised in that a 5-25% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran.

After adding the 4,6-dimethoxy-pyrimidine-2-isocyanate, the reaction mixture is stirred until conversion is complete. This process is preferably carried out at a temperature of 40-50°C. The J-modification obtained can be separated from the reaction mixture by filtration.

The process for the preparation of the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, is characterised in that a 5-25% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, then filtered, and the residue of filtration (J-modification) is subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

After adding the 4,6-dimethoxy-pyrimidine-2-isocyanate, the reaction mixture is stirred until conversion is complete. For drying in this process variant, a temperature of 40-60°C and a pressure of 0.02 to 0.06 bars are preferred.

The process for the production of the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, is characterised in that either the essentially amorphous form (A-modification) is exposed to an atmosphere of 98% relative humidity, or the K-modification is mixed with water in a ratio of water to K-modification of 0.1 : 1 to 0.4 : 1, then filtered, and the residue of filtration subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

When producing the C-modification, the ratio of water to K-modification may vary from 0.1 : 1 to 0.4 : 1, a ratio of 0.1 : 1 to 0.3 : 1 being preferred in particular. The addition of water may take place at a temperature of 0-60°C, most preferably at a temperature of 5-40°

C. Drying of the C-modification is preferably effected at a temperature of 40-60°C and at a pressure of 0.02-0.06 bars.

The C-modification may be advantageously produced whereby N-[(4,6-dimethoxy-2-pyrimidinyl)carbamoyl]-3-(2,2,2-trifluoro-ethoxy)-pyridine-2-sulfonamide is added to a solution of aqueous sodium hydroxide, afterwards it is concentrated by evaporation under vacuum at a temperature of 50°C, the residue thus obtained is stirred up with diethyl ether, filtered, dried at temperatures of ≥120°C and the essentially amorphous salt thus obtained (A-modification) is then exposed to an atmosphere of 98% relative humidity.

The process for the preparation of the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, is characterised in that a 5-25% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 0-30°C to a 10-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, and subsequently 1-20 molar equivalents of water, based on the 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt, are added.

In this variant, the addition of 2-5 molar equivalents of water is preferred in particular.

The process for the production of the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, is characterised in that water is added to the compound of formula I, in which M is sodium, n is 1 and L, r and s are defined as in formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, then filtration takes place and the residue of filtration is dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

A preferred variant of the process according to the invention for the production of the B-modification is characterised in that water is added to the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (K-modification), or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification) or to the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1 (I-modification), or to the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1 (C-modification), in a ratio of water to the K, J, I or C modification of 0.5 : 1 to 20 : 1, then

filtration takes place and the residue of filtration is subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

The temperature during the water addition may vary from 0-80°C. A temperature of 5-40°C is preferred in particular. The residue of filtration may be dried at temperatures of 30-90°C and at a pressure of 0.01 to 0.1 bars, preferably at a temperature of 40-60°C and at a pressure of 0.02-0.06 bars. It is most advantageous to mix the suspension with seed crystals of the B-modification in order to accelerate crystal growth.

The compounds of formula I may be used as herbicides in unmodified form, i.e. as obtained in the synthesis. However, they are preferably processed in conventional manner with the excipients that are customary in formulation technology, e.g. into directly sprayable or dilutable solutions, wettable powders, soluble or dispersible powders, soluble or dispersible granulates, dusts, and also so-called non-aqueous flowables. A composition which is especially preferred according to the invention is present in the form of soluble or dispersible granulates and contains crystal modification B as the compound of formula I.

Suitable formulations for the compounds of formula I are described for example in WO 97/34485 on pages 9 to 13. As with the type of agents, the methods of application such as spraying, atomising, dusting, wetting, scattering or pouring, are selected in accordance with the intended objectives and the prevailing circumstances.

The formulations, i.e. the agents, preparations, or compositions containing the active ingredient of formula I or at least one active ingredient of formula I and usually one or more solid or liquid formulation assistants, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with said formulation auxiliaries, typically solvents or solid carriers. Surface-active compounds (surfactants) may additionally be used for preparing the formulations. Examples of solvents and solid carriers are described in WO 97/34485 on page 6.

Depending on the type of active ingredient of formula I to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants and surfactant mixtures having good dispersing and wetting properties.

Examples of suitable anionic, nonionic, and cationic surfactants are listed for example in WO 97/34485 on pages 7 and 8.

Also the surfactants customarily for the art of formulation and described, *inter alia*, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch" (Handbook of Surfactants), Carl Hanser Verlag, Munich/Vienna, 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81 are suitable for manufacture of the herbicides according to the invention.

The herbicidal formulations will as a rule contain from 0.1 to 99 % by weight, preferably from 0.1 to 95% by weight, of herbicide, from 1 to 99.9% by weight, preferably from 5 to 99.8 % by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant. Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations. The compositions may also contain further ingredients, such as stabilisers, e.g. where appropriate epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil, or soybean oil), antifoams, typically silicone oil, preservatives, viscosity regulators, binders, and tackifiers, as well as fertilisers or other chemical agents.

The compounds of formula I are usually applied with success to the plants or the locus thereof in concentrations of 0.001 to 0.5 kg/ha, preferably 0.005 to 0.25 kg/ha. The concentration required to achieve the desired action can be determined by experimentation. It will depend on the type of action, the development stage of the cultivated plant and of the weed, as well as on the application (locus, time, method), and as a result of these variables can vary over a wide range.

The compounds of formula I have excellent herbicidal and growth inhibiting properties, which make them suitable for application in crops of cultivated plants, especially in cereals, cotton, soybeans, sugar beet, sugar cane, plantations, rape, maize, and rice, and for the non-selective control of weeds. Crops will also be understood to mean those crops that have been made tolerant to herbicides or classes of herbicides by conventional breeding or genetic engineering methods. The weeds to be controlled may be monocot as well as dicot

weeds, typically *Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola*, and *Veronica*.

The compounds of formula I may also be used in combination with a co-herbicide. Suitable co-herbicides are, for example, ametryn, atrazine, hexazinone, asulam, diuron, 2,4-D, halosulfuron, fluometuron, prometryn, metolachlor, α-metolachlor, norflurazon, pyrithiobac-sodium, DSMA, MSMA, trifluralin, pendimethalin, bromoxynil, glyphosate, glufosinate and clomazone.

The invention is illustrated by the following non-limitative Examples.

Formulation examples

F1. Coated granulates	a)	b)	c)
Active ingredient of formula I	0.1 %	5 %	15 %
Polyethylene glycol mw 200	1.0 %	2 %	3 %
Highly dispersed silicic acid	0.9 %	1 %	2 %
Inorganic carrier (Ø 0.1–1 mm) such as $CaCO_3$ or SiO_2	98.0 %	92 %	80 %

The finely ground active substance is uniformly applied in a mixer to the carrier moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

F2. Extruder granulates	a)	b)	c)	d)
Active ingredient of formula I	0.1 %	3 %	5 %	15 %
Sodium ligninsulfonate	1.5 %	2 %	3 %	4 %
Carboxymethylcellulose	1.4 %	2 %	2 %	2 %
Kaolin	97.0 %	93 %	90 %	79 %

The compound is mixed and ground with the adjuvants, and the mixture is moistened with water. This mixture is extruded and then dried in a stream of air.

F3. Dusts	a)	b)	c)
Active ingredient of formula I	0.1 %	1 %	5 %
Talc	39.9 %	49 %	35 %
Kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding on a suitable mill.

Example F4: Preparation of a wettable granulate of the compound of formula I:

The following substances are admixed and subsequently ground using a conventional mill.

75 %	A-crystal modification of the compound of formula I
4 %	dibutylnaphthalenesulfonic acid sodium salt
8 %	sodium lignin sulfonate
0.5 %	silicone defoamer
ad 100 %	silicon dioxide

The mixture is subsequently mixed with 22-26 % by weight water and granulated. After drying on a commercial continuous drier to a residual moisture of < 4.5 %, the granulate obtained is sieved (vibration/tumbler sieve) to a grain size of 0.4 to 1.6 mm. Granulates are obtained, which contain the compound of formula I as the C-crystal modification.

Example F5: Preparation of a wettable granulate of the compound of formula I:

The following substances are admixed and subsequently ground using a conventional mill.

75 %	B-crystal modification of the compound of formula I
4 %	dibutylnaphthalenesulfonic acid sodium salt
8 %	sodium lignin sulfonate
0.5 %	silicone defoamer
ad 100 %	silicon dioxide

The mixture is subsequently mixed with 18-20% by weight water and granulated. After drying on a commercial continuous drier to a residual moisture of < 4.5 %, the granulate obtained is sieved (vibration/tumbler sieve) to a grain size of 0.4 to 1.6 mm. Granulates are obtained, which contain the compound of formula I as the B-crystal modification.

Example F6: Preparation of a wettable granulate of the compound of formula I:

The following substances are admixed and subsequently ground using a conventional mill.

75 %	K-crystal modification of the compound of formula I
4 %	dibutylnaphthalenesulfonic acid sodium salt
8 %	sodium lignin sulfonate
0.5 %	silicone defoamer
ad 100 %	silicon dioxide

The mixture is subsequently mixed with 43-48% by weight water and granulated. After drying on a commercial continuous drier to a residual moisture of < 4.5 %, the granulate obtained is sieved (vibration/tumbler sieve) to a grain size of 0.4 to 1.6 mm. Granulates are obtained, which contain the compound of formula I as a mixture of the B-crystal modification and the C-crystal modification.

The X-ray powder pattern indicates the d-values (interlattice plane intervals), the associated intensities of the X-ray reflexes and the angle of refraction 2theta (apparatus-specific) of the corresponding crystal modification.

Measurement of the X-ray powder pattern was effected with an Enraf-Nonius Guinier camera FR 552 using CuKalpha1 radiation. The diagrams recorded on X-ray film were evaluated on a Johansson Line-Scanner LS-18 using Scanpi-Software.

Preparation Examples:

Example P1: Preparation of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification):

A solution of 40 g of 4,6-dimethoxy-pyrimidine-2-isocyanate in 300 g of tetrahydrofuran (water-free) is added at a temperature of 40-45°C to a suspension of 59 g of 3-(2-trifluoroethoxy)-pyridin-ylsulfonamide sodium salt in 210 g of water-free tetrahydrofuran.

The reaction mixture is subsequently stirred at a temperature of 40°C until conversion is complete. The J-modification is finally obtained by filtering and washing with water-free tetrahydrofuran.

Table X1: X-ray powder pattern of modification J:

2θ[degree]	d[Å]	Intensity
5.6	15.7	weak
8.6	10.2	very stark
10.7	8.2	weak
11.3	7.8	weak
12.1	7.3	weak
13.1	6.7	weak
13.6	6.5	very weak
14.4	6.2	average
15.7	5.64	very weak
16.0	5.53	weak
16.3	5.42	weak
17.4	5.09	weak
17.9	4.96	average
18.2	4.86	very weak
19.3	4.60	average
20.3	4.37	average
21.0	4.24	weak
21.6	4.11	very stark
22.5	3.95	very weak
22.8	3.90	weak
23.3	3.81	very weak
24.0	3.71	average
24.5	3.62	weak
25.3	3.52	very weak
26.0	3.43	stark
26.4	3.37	weak
26.8	3.32	very weak
27.3	3.27	weak
30.4	2.94	very weak
31.7	2.82	average

Example P2: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (K-modification):

The K-modification is obtained by drying the J-modification of example P1 at a temperature of 60°C and at a pressure of 0.04 bars. This crystal form is water-free and solvent-free: thermogravimetric measurement at 175°C shows a weight loss of less than 0.1 % by weight.

Table X2: X-ray powder pattern of modification K:

2θ[degree]	d[Å]	Intensity
6.6	13.4	weak
8.8	10.1	very weak
9.5	9.3	very strong
11.4	7.8	weak
12.9	6.9	very weak
13.3	6.7	very weak
15.7	5.63	very weak
16.6	5.35	average
19.0	4.66	weak
20.0	4.44	very weak
20.4	4.35	weak
21.5	4.12	strong
22.6	3.94	strong
22.9	3.87	very weak
23.7	3.76	weak
24.6	3.61	average
25.5	3.49	very weak
26.2	3.40	very weak

Example P3: Preparation of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1 (I-modification):

A solution of 19.9 g of 4,6-dimethoxy-pyrimidine-2-isocyanate in 350 g of tetrahydrofuran (water-free) is added at a temperature of 25 °C to a suspension of 34.2 g of 3-(2-trifluoroethoxy)-pyridin-ylsulfonamide sodium salt in 200 ml of water-free tetrahydrofuran. The reaction mixture is stirred at a temperature of 25°C until conversion is complete. Then,

10 g of water are added and the mixture stirred for 18 hours. The I-modification is finally obtained by filtering and washing with water-free tetrahydrofuran.

Table X3: X-ray powder pattern of modification I:

2θ[degree]	d[Å]	Intensity
7.6	11.6	weak
9.0	9.8	very weak
11.0	8.0	very strong
11.6	7.6	average
13.3	6.7	strong
13.7	6.4	very weak
14.0	6.3	weak
14.4	6.1	very weak
15.3	5.80	average
15.6	5.66	very weak
16.2	5.47	strong
17.3	5.12	very weak
17.4	5.08	very weak
18.3	4.84	weak
18.6	4.76	weak
19.8	4.47	strong
20.1	4.40	weak
21.1	4.21	average
21.2	4.19	average
21.4	4.15	very weak
22.2	4.00	very weak
22.6	3.93	very weak
23.2	3.84	average
23.9	3.72	very strong
24.8	3.58	average
25.3	3.52	average
26.9	3.32	very weak
27.2	3.28	very weak

2θ[degree]	d[Å]	Intensity
27.5	3.25	very weak
28.7	3.11	very weak
29.0	3.07	very weak
30.2	2.95	very weak
31.2	2.86	weak
31.7	2.82	very weak
32.6	2.75	very weak
34.9	2.57	weak
36.0	2.49	very weak

Example P4: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1 (B-modification):

The B-modification is obtained selectively by suspending 100 g of the K-modification prepared in example P2 in 230 g of water for 15 minutes, then seeding preferably with 1-3 g of seed crystals of the B-modification, and stirring the suspension at a temperature of 20-25 °C until transformation is complete. The suspension is subsequently filtered and the residue of filtration dried at a temperature of 60°C and at a pressure of 0.04 bars until attaining a constant weight.

Table X4: X-ray powder pattern of modification B:

2θ[degree]	d[Å]	Intensity
8.9	10.0	average
9.6	9.2	strong
10.3	8.6	very weak
11.0	8.1	weak
12.2	7.2	strong
12.9	6.9	strong
13.8	6.4	average
15.2	5.82	strong
15.4	5.75	strong
15.7	5.64	very strong

2θ[degree]	d[Å]	Intensity
16.0	5.53	very weak
17.3	5.13	average
17.8	4.97	very strong
19.1	4.65	average
20.6	4.30	very strong
21.0	4.22	weak
21.4	4.15	very weak
22.1	4.02	weak
22.5	3.94	weak
23.4	3.79	average
23.8	3.73	weak
24.2	3.68	average
24.6	3.61	weak
24.8	3.58	weak
25.3	3.52	very strong
26.0	3.42	very weak
26.4	3.37	weak
26.9	3.31	very weak
27.3	3.27	very weak
27.6	3.23	weak
28.0	3.18	average
28.9	3.08	very weak
29.4	3.03	very weak
30.3	2.95	very weak
31.2	2.87	strong
31.7	2.82	very weak
32.1	2.79	very weak
32.7	2.73	very weak
33.4	2.68	very weak
33.8	2.65	very weak
34.0	2.63	very weak
34.5	2.60	weak

2θ[degree]	d[Å]	Intensity
34.9	2.57	weak

The crystals forms A, C, F, I and J can also be transformed into the B form in analogous manner. In doing so, these crystal forms may also still be moist with solvent. In this case, the amount of water can be increased slightly.

Example P5: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (C-modification):

100 g of the K-modification produced in example P2 are mixed with 20 g of water for the duration of 3 hours and subsequently dried at a temperature of 60°C and at a pressure of 0.04 bars.

Table X5: X-ray powder pattern of modification C:

2θ[degree]	d[Å]	Intensity
6.7	13.1	average
8.1	11.0	very strong
10.1	8.8	weak
11.4	7.7	very strong
12.2	7.2	very strong
12.7	7.0	weak
13.9	6.4	weak
14.3	6.2	strong
14.9	5.96	weak
15.0	5.90	weak
15.7	5.64	strong
16.2	5.47	weak
16.6	5.34	average
17.1	5.19	weak
18.5	4.79	weak
18.7	4.74	average
19.1	4.64	very weak

2θ[degree]	d[Å]	Intensity
19.5	4.55	strong
19.9	4.47	weak
20.4	4.35	strong
20.8	4.26	average
21.5	4.13	weak
21.9	4.06	very weak
22.7	3.92	very strong
23.0	3.87	weak
23.5	3.79	very strong
24.2	3.67	weak
24.6	3.61	average
24.9	3.58	strong
25.7	3.47	weak
26.9	3.32	very weak
27.5	3.24	average
28.4	3.14	weak
28.6	3.12	weak
29.1	3.07	weak
29.3	3.04	strong
30.1	2.97	very weak
30.6	2.92	very weak
31.0	2.88	weak
31.7	2.82	weak
32.3	2.77	very weak
32.7	2.74	very weak
33.3	2.69	weak
33.7	2.66	very weak

Example P6: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, in essentially amorphous form (A-modification):

1.56 g of N-[(4,6-dimethoxy-2-pyrimidinyl)carbamoyl]-3-(2,2,2-trifluoroethoxy)-pyridin-2-sulfonamide are added at a temperature of 20°C to a solution of 40 ml of aqueous 0.1 N

sodium hydroxide. The reaction mixture is stirred for 18 hours at a temperature of 20°C. The residue obtained after concentrating by evaporation under vacuum at a temperature of 50° C is subsequently stirred with ether and filtered. The A-modification is obtained by drying the filtrate at elevated temperatures (>120°C).

Example P7: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0 (C-modification) from the A-modification:

Crystals of the A-modification are exposed to an atmosphere of 98% relative humidity for 4 hours at a temperature of 20°C. The C-modification is obtained with the crystallographic data given in example P5.

Example P8: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 2, L is dioxane and s is 0 (G-modification):

15 g of the A-modification produced e.g. as in example P6 are stirred in 85 g of dioxane for 2½ days at a temperature of 20°C and the mixture subsequently filtered. After filtration, the G-modification is obtained as the residue of filtration with the X-ray crystallographic data given in Table X8.

Table X8: X-ray powder pattern of modification G:

2θ[degree]	d[Å]	Intensity
5.8	15.3	strong
7.0	12.7	very weak
8.4	10.5	weak
11.1	7.9	average
12.8	6.9	average
13.4	6.6	very weak
14.3	6.2	very strong
14.9	5.96	average
17.4	5.08	average
17.8	4.98	weak
18.3	4.84	average

2θ[degree]	d[Å]	Intensity
19.3	4.60	average
19.7	4.51	average
19.8	4.47	very weak
20.8	4.27	weak
21.0	4.23	average
22.3	3.98	average
22.7	3.91	average
23.3	3.81	weak
23.9	3.71	strong
24.4	3.65	average
24.9	3.57	weak
25.4	3.50	average
26.2	3.39	very weak
26.7	3.33	weak
28.9	3.08	very weak
29.5	3.02	very weak
30.5	2.93	weak

Example P9: Preparation of the compound of formula I, in which M is sodium, n is 1, r is 1, L is dioxane and s is 0 (F-modification):

The F-modification is obtained by exposing the G-modification produced in example P8 to an atmosphere of 50% relative humidity for a period of 8 days at a temperature of 20-25°C.

Table X9: X-ray powder pattern of modification G:

2θ[degree]	d[Å]	Intensity
6.0	14.7	very weak
7.0	12.6	very weak
8.1	10.9	average
11.4	7.8	average

2θ[degree]	d[Å]	Intensity
12.0	7.4	very weak
12.7	7.0	weak
13.4	6.6	weak
14.3	6.2	weak
16.2	5.45	strong
18.0	4.91	average
18.4	4.83	weak
18.6	4.76	very weak
20.8	4.28	very weak
21.7	4.10	weak
22.2	4.00	very weak
23.7	3.75	very strong
24.7	3.60	very weak

Biological Examples

Example B1: Post-emergent herbicidal action

The test plants are sown in standard soil in plastic pots in a greenhouse, and sprayed at the 2- to 3-leaf stage with an aqueous suspension of the test compounds of formula I prepared from a 25% wettable powder [example F3, b) of WO 97/34485] of the test compounds of formula I, at a dosage of 7.5 g/ha. The test plants are then further cultivated in the greenhouse under optimum conditions. After ca. 21 days test duration, the test is evaluated (100 = total damage, 0 = no damage). Table 1 shows the results obtained.

Table 1: Post-application on cotton

test plants	K-modification
cotton	15
Ipomea	90
Xanthium	100
Cassia	98

Example B2: Post-emergent herbicidal action

The test plants are sown in standard soil in plastic pots in a greenhouse, and sprayed at the 2- to 3-leaf stage with an aqueous suspension of the test compounds of formula I prepared from a 75% wettable granulate (example F4 for the A-modification or example F5 for the B-modification) of the test compounds of formula I, at a dosage of 7.5 g/ha. The test plants are then further cultivated in the greenhouse under optimum conditions. After ca. 21 days test duration, the test is evaluated (100 = total damage, 0 = no damage). Table 2 shows the results obtained.

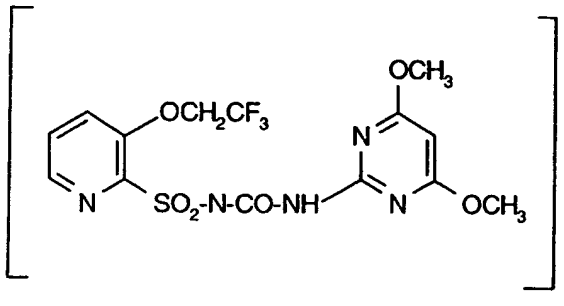
Table 2: Post-application on cotton

test plants	A-modification	B-modification
cotton	5	0
Ipomea	80	75

The same results are obtained by formulating the compounds of formula I in accordance with Examples F2 and F6 to F8 of WO 97/34485.

What is claimed is:

1. Compounds of formula I



$M^{n+} \bullet L_r \bullet [H_2O]_s$ (I),

wherein

M is an alkali metal or an alkaline earth metal;

n is 1 or 2;

r and s, independently of one another, are 0, ½, 1, 1½, 2, 2½ or 3; and

L is ethyl acetate, acetonitrile, dimethylsulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, methylene chloride, trichloromethane, trichloroethane, tetrahydrofuran, diethylether, 1,2-dimethoxyethane, dioxane, methyl-tert.-butylether, chlorobenzene, toluene or xylene, with the provision that r is other than 1½ if L is dioxane and s is 0.

2. Compounds of formula I according to claim 1, in which M is sodium, potassium, magnesium or calcium.

3. Compounds of formula I according to claim 1, in which L is dioxane, tetrahydrofuran or water.

4. Compounds of formula I according to claim 1, in which n is 1 and M is sodium.

5. Compounds of formula I according to claim 1, in which M is sodium, n is 1, r is 0 and s is 0.

6. Compounds of formula I according to claim 1, selected from

- the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 10.0/average; 9.2/strong; 8.6/very weak; 8.1/weak; 7.2/strong; 6.9/strong; 6.4/average; 5.82/strong; 5.75/strong; 5.64/very strong; 5.53/very weak; 5.13/average; 4.97/very strong; 4.65/average; 4.30/very strong; 4.22/weak; 4.15/very weak; 4.02/weak; 3.94/weak; 3.79/average; 3.73/weak; 3.68/average; 3.61/weak; 3.58/weak; 3.52/very strong; 3.42/very weak; 3.37/weak; 3.31/very weak; 3.27/very weak; 3.23/weak; 3.18/average; 3.08/very weak; 3.03/very weak; 2.95/very weak; 2.87/strong; 2.82/very weak; 2.79/very weak; 2.73/very weak; 2.68/very weak; 2.65/very weak; 2.63/very weak; 2.60/weak; 2.57/weak;

- the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0, characterised by the X-ray powder pattern with d[Å]/intensity: 5.7/weak; 10.2/very strong; 8.2/weak; 7.8/weak; 7.3/weak; 6.7/weak; 6.5/very weak; 6.2/average; 5.64/very weak; 5.53/weak; 5.42/weak; 5.09/weak; 4.96/average; 4.86/very weak; 4.60/average; 4.37/average; 4.24/weak; 4.11/very strong; 3.95/very weak; 3.90/weak; 3.81/very weak; 3.71/average; 3.62/weak; 3.52/very weak; 3.43/strong; 3.37/weak; 3.32/very weak; 3.27/weak; 2.94/very weak; 2.82/average;

- the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, characterised by the X-ray powder pattern with d[Å]/intensity: 13.4/weak; 10.1/very weak; 9.3/very strong; 7.8/weak; 6.9/very weak; 6.7/very weak; 5.63/very weak; 5.35/average; 4.66/weak; 4.44/very weak; 4.35/weak; 4.12/strong; 3.94/strong; 3.87/very weak; 3.76/weak; 3.61/average; 3.49/very weak; 3.40/very weak;

- the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 13.1/average; 11.0/very strong; 8.8/weak; 7.7/very strong; 7.2/very strong; 7.0/weak; 6.4/weak; 6.2/strong; 5.96/weak; 5.90/weak; 5.64/strong; 5.47/weak; 5.34/average; 5.19/weak; 4.79/weak; 4.74/average; 4.64/very weak; 4.55/strong; 4.47/weak; 4.35/strong; 4.26/average; 4.13/weak; 4.06/very weak; 3.92/very strong; 3.87/weak; 3.79/very strong; 3.67/weak; 3.61/average; 3.58/strong; 3.47/weak; 3.32/very weak; 3.24/average; 3.14/weak; 3.12/weak; 3.07/weak; 3.04/strong; 2.97/very weak; 2.92/very weak; 2.88/weak; 2.82/weak; 2.77/very weak; 2.74/very weak; 2.69/weak; 2.66/very weak; and

- the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, characterised by the X-ray powder pattern with d[Å]/intensity: 1.6/weak; 9.8/very weak; 8.0/very strong; 7.6/average; 6.7/strong; 6.4/very weak; 6.3/weak; 6.1/very weak; 5.80/average; 5.66/very weak; 5.47/strong; 5.12/very weak; 5.08/very weak; 4.84/weak; 4.76/weak; 4.47/strong; 4.40/weak; 4.21/average; 4.19/average; 4.15/very weak; 4.00/very weak; 3.93/very weak; 3.84/average; 3.72/very strong; 3.58/average; 3.52/average; 3.32/very weak; 3.28/very weak; 3.25/very weak; 3.11/very weak; 3.07/very weak; 2.95/very weak; 2.86/weak; 2.82/very weak; 2.75/very weak; 2.57/weak; 2.49/very weak.

7. A compound of formula I according to claim 1, wherein
M is sodium, n is 1, r is 0 and s is 0 (K-modification), produced by drying the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0 (J-modification), at a temperature of 35°C to 65°C in a vacuum.
or wherein
M is sodium, n is 1, r is 0 and s is 1 (C-modification), produced by
either
contact of the essentially amorphous form (A-modification) by air of 98% relative humidity or mixing the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, with water in a ratio of water to the K-modification of 0.1 : 1 to 0.4 : 1 and separating and drying the product obtained at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;
or wherein
M is sodium, n is 1, r is 0 and s is 1 (B-modification), produced by
adding water to the compound of formula I, in which M is sodium, n is 1 and L, r and s are defined as in formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, then filtering and the drying the residue of filtration at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

8. A method for the preparation of compounds of formula I according to claim I, whereby in order to produce the J-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is ½ and s is 0, a 5-35% by weight solution of 4,6-dimethoxy-

pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran;
in order to produce the K-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 0, a 5-35% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 35-65°C to a 15-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, then filtered, and the residue of filtration (J-modification) is subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;
in order to produce the C-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, either the essentially amorphous form (A-modification) is exposed to an atmosphere of 98% relative humidity, or the K-modification is mixed with water in a ratio of water to K-modification of 0.1 : 1 to 0.4 : 1, then filtered, and the residue of filtration subsequently dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars;
in order to produce the I-modification of the compound of formula I, in which M is sodium, n is 1, L is tetrahydrofuran, r is 1 and s is 1, a 5-35% by weight solution of 4,6-dimethoxy-pyrimidine-2-isocyanate in water-free tetrahydrofuran is added at a temperature of 0-30°C to a 10-35% by weight suspension of 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt in water-free tetrahydrofuran, and subsequently 1-20 molar equivalents of water, based on the 3-(2-trifluoroethoxy)-pyridinyl-sulfonamide sodium salt, are added; and
in order to produce the B-modification of the compound of formula I, in which M is sodium, n is 1, r is 0 and s is 1, water is added to the compound of formula I, in which M is sodium, n is 1 and L, r and s are defined as in formula I, in a ratio of water to this compound of 0.5 : 1 to 20 : 1, then filtration takes place and the residue of filtration is dried at a temperature of 30-90°C and at a pressure of 0.01 to 0.1 bars.

9. A herbicidal and plant growth inhibiting composition, which comprises a herbicidally effective amount of the compound of formula I on an inert carrier.

10. Composition according to claim 9, which contains a co-herbicide.

11. A method of controlling undesirable plant growth, which comprises treating the plants or the locus thereof with a herbicidally effective amount of an active ingredient of formula I or of a composition containing such an active ingredient.

12. A method of inhibiting plant growth, which comprises treating the plants or the locus thereof with a herbicidally effective amount of an active ingredient of formula I or of a composition containing such an active ingredient.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D401/12 A01N47/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 41112 A (CIBA GEIGY AG ;FOERY WERNER (CH)) 6 November 1997 (1997-11-06) cited in the application the whole document	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 2000	11/07/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/EP 00/01627

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9741112 A	06-11-1997	AU 2696997 A	19-11-1997
		HR 970212 A	30-04-1998